4. The model of the atom

4.1 Thomson's model of the atom

Discovery of electron (J.J. Thomson), his measurement of $e/m$ (1897), and Millikans measurement of the charge of the electron (1909) implied that the majority of the mass of the atom was associated with positive charge.

How was this mass and positive charge distributed? Size of atom known to be $10^{-10}$m. "pudding model" - positively charged dough with electrons as raisins - it was suggested that the displacement of these from their equilibrium positions gives rise to simple harmonic motion - but this model gives wrong frequencies.

4.2 Geiger-Marsden experiment

- Other observations of Geiger- Marsden experiment were even more surprising:
  - Backscattering of some α-particles was observed (nearly 180 degrees)
  - Such a result conclusively rules out the "cake" model

4.2 Rutherford scattering

Rutherford explained these results, introducing a new physical model of the atom, as follows:

- Large deviations or scattering at large angles only possible if positive charge and mass located within a tiny fraction of the volume of the atom.
- The observed scattering becomes a straightforward electrostatics and kinetics problem.
  - Work through Example 38.5 - p 1321
  - If one assumes that the positive charge is located within a sphere at the centre of the atom, smaller than the size of the atom, then can compare the predictions of this model to the experimental data.

4.2 (ctd) - Rutherford scattering

-In this model the rate of scattering at high angles, or the probability of scattering into high angles, is related to the radius of the sphere containing the positive charge and concentrated mass.
-Examples: scattering of a 5.0 MeV α-particle from a gold nucleus.

With $θ$ determined for a given impact parameter $b$, then calculate the fraction of particles with different impact parameters. Compare to experiment.

On the calculation of Rutherford scattering see http://hyperphysics.phy-astr.gsu.edu/hbase/rutsc.html
### 4.2 (ctd) Rutherford's classical model of the atom

In the classical picture of an electron orbit, the electron has kinetic energy due to its motion. However, it does not leave the atom because it is bound to the positively charged central nucleus, and hence feels an attractive (centripetal) force towards that nucleus.

![Diagram of Rutherford's classical model of the atom](image)

This is the picture suggested by Rutherford after the Geiger-Marsden experiment.

### 4.2 Rutherford's model of the atom

Geiger–Marsden experiment tells us the following, necessary for any new theory:

**Ingredients**

- **Atom** essentially empty, nucleus occupies only about $10^{-12}$ of total volume of atom, but all the positive charge and 99.95% of the total mass of the atom.
- **Discrete energy levels**
- **Mini-solar system?** (Rutherford's picture)

But orbiting electrons must radiate (they clearly undergo continuous acceleration, and accelerated charges radiate energy),

$\Rightarrow$ a continuous loss of energy; any such electrostatic orbit is not stable; further, with any possible choice of orbit, there is a continuous range of orbital frequencies and this would imply a continuous spectrum.

**significant problems for theory**

How is this addressed?

### 4.3 Bohr's model of the atom

**Bohr postulates (1911-1913)**

- Electrons move in **stable circular orbits** without emission of radiation.
- Definite energy associated with each stable orbit.
- **Radiation** only for transition from one orbit to another.

Radiation involves one photon:

$$ \Delta E = h \cdot \nu = E_i - E_f $$

- **Stable orbits** characterized by quantized angular momentum.

**Angular momentum:**

$$ \vec{L} = m \cdot \vec{r} \times \vec{v} $$

Circular motion:

$$ \vec{r} \perp \vec{v} $$

**Quantization:**

$$ L_n = m \cdot r_n \cdot v_n = n \cdot \frac{h}{2\pi} = n \cdot \hbar $$

$n$ is principal quantum number, $n = 1, 2, 3, \ldots$

### 4.3 (ctd) - Bohr's model of the atom

**Model of Hydrogen atom:** circular motion of one electron about positive nucleus

- **Radius of circular motion** $r_n$ - distance between charges
- Coulomb force between +ve and -ve charges:

$$ F_r = -\frac{1}{4\pi \varepsilon_0} \frac{e^2}{r_n^2} $$

- **Newton's 2nd law** - circular motion:

$$ F_r = m \cdot a = m \frac{v_n^2}{r_n} $$

- Set

$$ F_r = F_a = \frac{1}{4\pi \varepsilon_0} \frac{e^2}{r_n^2} = m \frac{v_n^2}{r_n} $$

- From

$$ m \cdot r_n \cdot v_n = n \cdot \hbar 
\Rightarrow r_n = \frac{n \cdot \hbar}{m \cdot v_n} $$

- Obtain:

$$ v_n = \frac{1}{\varepsilon_0} \frac{e^2}{2 \cdot n \cdot \hbar} 
\text{ and } 
\frac{r_n}{\hbar} = \frac{n^2 \cdot \hbar^2}{\varepsilon_0 \cdot m \cdot e^2} $$
### 4.3 (ctd) - Bohrs model of the atom

**Bohr Model:**

\[ r_n = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{n^2} \]

Minimum radius corresponds to \( n = 1 \)

\[ r_1 = a_0 = 4\pi\varepsilon_0 \frac{\hbar^2}{e^2} \approx 5.29 \times 10^{-11} \text{m} \]

Thus diameter \( \sim 10^{-10} \text{m} \)

The radius is often written in terms of \( a_0 \), the Bohr radius:

\[ r_n = n^2 \cdot a_0 \]

**Orbital speed** \( v_1 = 2.19 \times 10^6 \text{m.s}^{-1} \), so no relativistic treatment needed

### 4.3 (ctd) - Bohrs model of the atom

**Energy levels in Hydrogen atom:**

Sum of kinetic and potential energy terms:

\[ E_n = K_n + U_n = -\frac{m e^4}{8\varepsilon_0^2 \hbar^2} < 0 \]

Potential energy set to zero when electron infinitely far from nucleus. As the total energy is \(<0\) can consider the electron to be **bound** with respect to an electron at an infinite distance from the nucleus.

**Change in energy level from \( n = i \) to \( n = f \):**

\[ \Delta E = h\nu = E_f - E_i = \frac{m e^4}{8\varepsilon_0^2 \hbar^2} \left( \frac{1}{f^2} - \frac{1}{i^2} \right) \]

This agrees with the Rydberg formula where we set \( R \) as:

\[ R = \frac{m e^4}{8\varepsilon_0^2 \hbar^2 c} = 1.097 \times 10^{-7} \text{m}^{-1} \]

Agrees perfectly with the value of \( R \) obtained from the Hydrogen spectrum

### 4.3 (ctd) - Bohrs model of the atom

**Define the ionization energy as the energy required to go from \( n = 1 \) to \( n = \infty \):**

The predicted ionization energy agrees with experiment (and \( R \))

\[ E_{\text{ionization}} = \frac{1}{\varepsilon_0} \frac{m e^4}{8\hbar^2} = 13.606 \text{eV} \]

Note we see that this works well for Hydrogen, but not exactly, one other detail is necessary:

**Reduced mass** - instead of \( m \) the mass of the electron, must use the reduced mass given by:

\[ m_r = \frac{m_e m_p}{m_e + m_p} \]

\[ m_r = 1836 \cdot m_e \]

\[ m_r = 99945 \cdot m_e \]

... now giving an exact fit.

What about other spectra?

### 4.4 Hydrogenic atoms

**What about spectra from other atoms:**

Simple Bohr model explains hydrogen-like spectra very accurately

Where charge of nucleus is \(+Ze\), then obtain

\[ F_r = \frac{1}{4\pi\varepsilon_0} \frac{Z e^2}{r_n^2} \]

Solving for \( v_n \) and \( r_n \):

\[ v_n = \frac{1}{a_0} \frac{2 \cdot e^2}{n^2 \cdot \hbar} \]

\[ r_n = \frac{e_0}{\pi \cdot m \cdot Z \cdot e^2} \]

And the energy levels become:

\[ E_n = -\frac{1}{\varepsilon_0} \frac{m \cdot Z^2 \cdot e^4}{4 \cdot n^2 \cdot \hbar^2} < 0 \]

For He\(^{2+}\) (\( Z = 2 \)), the ionization energy is

4 times greater \( \Rightarrow 54.4 \text{eV} \)

For U\(^{92+}\) (\( Z = 92 \)) \( \Rightarrow 115 169 \text{eV} \)

(See graph on binding energies)
4.5 Non-Hydrogenic atoms

The simple Bohr model explains hydrogen-like spectra, but can also explain alkali spectra with modifications.

For hydrogen-like systems

\[ E_n = \frac{Z^2 \cdot R \cdot h \cdot c}{n^2} \quad E_n = -\frac{m \cdot Z^2 \cdot e^4}{\epsilon_0^2 \cdot 4 \cdot n^2 \cdot r^2} \]

Consider the spectrum of lithium, sodium, potassium etc.

Their electronic structure is simple with one electron outside completely filled inner shells. Outermost electron perceives a change of \( \sim +1 \) ft from the nucleus and inner electrons

Empirically describe the energy levels associated with changes in the principal quantum number \( n \) of this outermost electron as being:

\[ E_n = -\frac{R \cdot h \cdot c}{(n-\delta)} \]

where \( \delta \) is a "quantum defect" which characterises the series of spectral lines.

Rutherford scattering - inside the proton

Imagine repeating the Geiger-Marsden experiment but now firing electrons to probe inside the proton itself.

Several experiments through the 1950s, 60s, 70s and into the 1990s looked inside protons and discovered QUARKS

Deviations from the Rutherford scattering formulae gives support for quark hypothesis - from elastic scattering exps (1950s Hofstadter - 1961 Nobel prize)

...and then also from inelastic scattering experiments (1970s Kendall, Friedman, and Taylor - 1990 Nobel prize) helped prove that QUARKS exist

4.6 Bohr's model of the atom (again)

Bohr postulated that the angular momentum of the electron is quantised

Alternately bearing in mind deBroglie's relation (1924):

\[ \lambda = \frac{h}{p} \Rightarrow \lambda = \frac{h}{m \cdot v} \]

could postulate that the only possible orbits of the electron are those that satisfy a standing-wave condition for the electron wavelength:

\[ L = m \cdot v \cdot r = \frac{h \cdot r}{\lambda} \]

Giving:

\[ L = \frac{n \cdot h}{2 \pi} \]

How big can an atom get?

The size of the H atom with the electron in the lowest orbit is \( a_0 = 0.05 \) nm. An atom with the electron in an extremely high Rydberg state is much, much bigger!

\[ r_e = n^2 \cdot a_0 \]

Ground state, \( n=1-5 \Rightarrow \) diameters of 1-25 \( \times 10^{-10} \) m

What if \( n \) becomes very large? - then the energy of the state becomes very close to the ionization limit - only a small amount of (thermal) energy is enough to ionise the atom - collisions will do so easily

Go somewhere less dense to lower the rate of collisions, then choose an excitation energy just below the ionisation threshold to populate a state with high \( n \) value

See also http://physicaworld.com/cws/article/print/21590

Laboratory record for a Rydberg atom (Rice University, Texas, 2008)

\[ n \approx 306 \quad r_e = n^2 \cdot a_0 \Rightarrow r_{306} = 93,636 \cdot a_0 = 4.9 \mu m \]

See http://prl.aps.org/abstract/PRL/v100/i24/e243004

Record for a Rydberg atom observed in space (observed 2007)

\[ n \approx 1009 \quad r_e = n^2 \cdot a_0 \Rightarrow r_{1009} = 1,018,081 \cdot a_0 = 54 \mu m \]